

Western Research Institute

2009 Publications

Bullard, J.W., A.T. Pauli, E.J. Garboczi, and N.S. Martys, 2009, A Comparison of Viscosity-Concentration Relationships for Emulsions. *Journal of Colloid and Interface Science*, 330 (1): 186-193.

Abstract: Differential effective medium theory (D-EMT) has been used by a number of investigators to derive expressions for the shear viscosity of a colloidal suspension or an emulsion as a function of the volume fraction of the dispersed phase. Pal and Rhodes [R. Pal, E. Rhodes, *J. Rheol.* 33 (7) (1989) 1021–1045] used D-EMT to derive a viscosity–concentration expression for non-Newtonian emulsions, in which variations among different oil–water emulsions were accommodated by fitting the value of an empirical salvation factor by matching the volume fraction at which the ratio of each emulsion was experimentally observed to have a viscosity 100 times greater than that of the pure solvent. When the particles in suspension have occluded volume due to solvation or flocculation, we show that the application of D-EMT to the problem becomes more ambiguous than these investigators have indicated. In addition, the resulting equations either do not account for the limiting behavior near the critical concentration, that is, the concentration at which the viscosity diverges, or they incorporate this critical behavior in an ad hoc way. We suggest an alternative viscosity–concentration equation for emulsions, based on work by Bicerano and coworkers [J. Bicerano, J.F. Douglas, D.A. Brune, *J. Macromol. Sci., Rev. Macromol. Chem. Phys. C* 39 (4) (1999) 561–642]. This alternative equation has the advantages that (1) its parameters are more closely related to physical properties of the suspension and (2) it recovers the correct limiting behavior both in the dilute limit and near the critical concentration for rigid particles. In addition, the equation can account for the deformability of flexible particles in the semidilute regime. The proposed equation is compared to the equation proposed by Pal and Rhodes.

Huang, S-C., and W. Grimes, “Influence of Aging Temperature on Rheological and Chemical Properties of Asphalt Binders,” accepted for presentation and submitted for publication at the 2010 Transportation Research Board annual meeting.

Abstract: Four asphalts used in field pavement were laboratory PAV aged at several different temperatures for various lengths of time. The chemical (I.R. spectra) and rheological properties of these aged asphalts were compared. The results showed that the same PG graded asphalts from different crude sources show significant differences with respect to their rheological behavior and chemical properties after long-term oxidative aging. It was also found that asphalt per se has approximately the same aging rheological pattern regardless of the aging temperature. It was discovered that laboratory PAV aging at 80°C for 504 hours produced stiffer material than the same material subjected to the same PAV aging at 100°C for 100 hours. The plot of “G* versus phase angle” was found to be particularly useful for characterizing the asphalt binder rheology in terms of long-term aging characteristic. In addition, the aging shift factor, generated from aging master curve, was used to characterize the modulus changes with respect

to aging and also was used for the comparison of the effects of aging on different materials. Furthermore, the results indicated that there is a linear relationship between the change of rheological property and the change of chemical property (carbonyl index) with respect to long term aging. It was verified that sulfoxide is formed easily with aging. However, it can also decompose at longer aging times.

Miknis, F. P., and W. C. Schuster, "NMR Study of Hydrated Lime and Limestone in Polyphosphoric Acid Modified Bitumen," *Road Materials and Pavement Design*, in press.

Abstract: Phosphorous-31 NMR spectroscopy has been used to study the effect of hydrated lime and limestone fines on polyphosphoric acid (PPA)-modified bitumens. NMR spectra were acquired on bitumen samples that were first modified with PPA and on bitumen samples when hydrated lime was added before the PPA. In both cases the NMR spectra showed that calcium phosphates, primarily dibasic calcium phosphate (monetite), and calcium dihydrogen phosphate were formed as a result of an acid-base reaction between the PPA and the hydrated lime. Fourier Transform Infrared (FTIR) Spectroscopy showed that hydrated lime was still present in the bitumen after the PPA was neutralized by the hydrated lime. In another set of experiments in which a calcitic or a dolomitic limestone was substituted for hydrated lime, no reactions were observed between the limestones and the PPA.

Morris, J.M., S. Jin, B. Crimi, and A. Pruden, 2009, "Microbial Fuel Cell for Enhancing Anaerobic Biodegradation of Diesel," *Chemical Engineering Journal*, 146:161–167.

Abstract: Microbial fuel cell (MFC) technology can potentially be applied to enhance subsurface bioremediation of contaminants such as petroleum hydrocarbons by providing an inexhaustible source of terminal electron acceptors to a groundwater environment that is likely depleted in thermodynamically favorable electron acceptors such as oxygen and nitrate. Results indicate that anaerobic biodegradation of diesel range organics (compounds eluting with n-alkane markers ranging in size from C-8 to C-25) was significantly enhanced ($P=0.007$) in an MFC (82% removal) as compared to an anaerobically-incubated control cell (31% removal) over 21 days at 30°C, meanwhile, as much as 31 mW/m² cathode of power was generated during diesel degradation (as measured during a polarization curve experiment). The microbial consortium on the anode of a diesel-degrading MFC was characterized by cloning and sequencing 16S rRNA genes. The majority of the clone sequences showed > 98% similarity to bacteria capable of denitrification, such as *Citrobacter* sp., *Pseudomonas* sp., and *Stenotrophomonas* sp. The remaining clone sequences showed high similarity with organisms capable of using a wide range of electron acceptors, including sulfate, arsenate, and chlorinated inorganics. In particular, *Shewanella* sp. and *Alishewanella* sp. were found, which are typically capable of using multiple electron acceptors. This study suggests that MFC technology may be used for enhancing biodegradation of petroleum

contaminants in anoxic environments, thus, eliminating the need to amend terminal electron acceptors such as oxygen.

J.M. Morris, Fallgren, P.H., Jin, S., In press, Enhanced Denitrification through Microbial and Steel Fuel-Cell Generated Electron Transport, *Chem. Eng. J.* Volume 153, Issues 1-3, 1 November 2009, Pages 37-42

Abstract: Enhancement of nitrate reduction was studied in a two-chambered microbial fuel cell (MFC) and a similar abiotic fuel cell (steel fuel cell or SFC) with an oxidizable steel wool anode and catalyst-free stainless steel mesh cathode. In the MFC and SFC systems, nitrate was reduced in the cathode chamber at 11.4 or 40.0mgnitrate/L/day, respectively. The MFC utilized petroleum compounds in refinery wastewater as the electron donor and the SFC utilized steel wool as the electron donor. Oxidation of the petroleum compounds in the MFC and steel wool in the SFC caused electron flow from the anode to the cathode, where nitrate was reduced. Nitrate reduction was significantly ($P < 0.001$) higher in SFCs with non-sterile groundwater in the cathode chambers and the flow of electrons to the cathode stimulated microbial growth. Our results suggest that both MFC and SFC designs could serve as electron source for nitrate reduction at the cathode. Particularly the SFC could be an innovative low-cost, low-maintenance alternative for in-situ remediation of nitrate-contaminated groundwater.

J.M. Morris, S. Jin, In Press, Influence of NO₃ and SO₄ on Power Generation from Microbial Fuel Cells, *Chem. Eng. J.* Volume 153, Issues 1-3, 1 November 2009, Pages 127-130

Abstract: Potential competition in terms of electron transfer from bacteria to electron acceptors such as nitrate (NO₃) and sulfate (SO₄) or the anode of a microbial fuel cell (MFC) was investigated to determine how alternative electron acceptors would influence power generation in an MFC. The cell voltage was not initially affected when these electron acceptors were introduced into the MFCs. However, the presence of NO₃ decreased the CE of the MFC compared to the injections of SO₄ or control salt (sodium chloride). This suggests that the growth of nitrate-reducing bacteria independent of the microbial populations on the MFC anode were not utilizing the anode as an electron acceptor, rather, they were consuming organic carbon in the anodic chamber of the MFC, resulting in a decrease of the CE of this MFC with no immediate impact on power output. This suggests that the bacterial consortium in the nitrate-MFC still preferred the anode over nitrate as the electron acceptor, although the theoretical reduction voltage of nitrate (+0.74V) is higher than the reduction voltage in an MFC air cathode (as high as +0.425). These results are useful when considering whether MFC technology can be applied in situ to enhance biodegradation of organic contaminants in the presence of alternative electron acceptors.

Sui, C., M. J. Farrar, W. H. Tuminello and T. F. Turner, "A New Technique for Measuring Low-Temperature Properties of Asphalt Binders with Small Amounts of Material," accepted for presentation and submitted for publication at the 2010 Transportation Research Board annual meeting.

Abstract: A new technique, which uses 4 mm parallel plates on a dynamic shear rheometer (DSR) with machine compliance corrections, was developed to measure low-temperature properties of asphalts. Test temperatures have been demonstrated to as low as -40 °C. The test method requires only about 25 mg of material instead of 15 g for the bending beam rheometer (BBR). Also, no specimen pre-molding is needed and a relatively low temperature (60 ~ 70 °C) is required to load the samples into the measuring system. The key to the new technique is the correction for errors due to machine compliance. Two types of machine compliance correction were applied to the dynamic frequency sweep data in this work. The effects of the machine compliance on the measured low temperature properties, the reproducibility of data, the consistency among the data collected on different sizes of plates after machine compliance corrections, and the comparison between the corrected data from DSR and converted BBR data were investigated. The results show that this new technique is a reliable, rapid, and simple to perform test method, which allows for analysis of low-temperature properties of asphalt binder as well as extracted samples from pavements and other materials such as cold-mix asphalt (CMA) and emulsion residue that require low temperature operations and small samples.

Zhang, T., L. T. Fan, W. P. Walawender, M. Fan, A. E. Bland, T. Zuo, and D. W. Collins, "Hydrogen Storage on Carbon Adsorbents: Review," *Environanotechnology* (book), Eds., M. Fan, C. P. Huang, R. B. Slimane, I. G. Wright, A. E. Bland, and Z. L. Wang, Elsevier, in press.

Abstract: Hydrogen energy has been extensively explored as a potential solution to the increase in global energy demand and global warming due to greenhouse gas emissions. Significant advances have been made in the on-board storage of H₂ for its application as a transportation fuel. Three major approaches are available. They include pressurization of H₂ in high-pressure vessels; liquefaction of H₂ at the cryogenic temperature; and materials-based H₂ storage. Although none has succeeded in reaching the target densities established by the US Department of Energy, the most promising appears to be the last. It is inherently safer and is potentially more energy efficient than the first two. While various materials have received significant attention, carbon adsorbents seem to have the greatest potential: They are light, inexpensive, and ideal from the point of view of gravimetric requirements of the use in fuel cells for automobiles. Moreover, the industry has substantial expertise in the production of carbon adsorbents with effective control of their micro- and nano-structures for their industrial-scale production. Consequently, the hydrogen storage on carbon adsorbents, including activated carbons, carbon nanofibers, and single-wall as well as multi-wall carbon nanotubes, has been extensively investigated. This review focuses on the recent studies of hydrogen adsorption on these carbon adsorbents.

Zhang, T., and L. T. Fan, "Significance of Dead-state-based Thermodynamics in Designing a Sustainable Process," *Design for Energy and the Environment - Proceedings of the Seventh International Conference on the Foundations of Computer-Aided Process Design*, Eds., M. M. El-Halwagi and A. A. Linninger, CRC Press, Boca Raton, FL, pp.233-241, 2010.

Abstract: The standard state of thermodynamics is regarded to be in thermal and mechanical equilibrium with the environment having the temperature and pressure of 298.15 K and 1 atm, respectively. In contrast, the dead state, or extended standard state, is defined such that it is not only in thermal and mechanical equilibrium with the environment but also in chemical equilibrium with the environment. Consequently, the enthalpy of formation and free-energy of formation of the substance at the dead state are invariably non-negative. As such, the energy and available energy balances can be executed in a straightforward manner around any given system (process), or arbitrary segment of the system. This gives rise to the energy loss from and the available energy consumption, i.e., exergy dissipation, of the process or segment of the process. Thus, dead-state-based thermodynamics renders it possible to carry out the multi-scale thermodynamic analysis of a process necessary for the assessment of its sustainability on the uniformly consistent platform at any desired level of details. This is not the case with the standard-state-based thermodynamics: The standard enthalpy of formation and free-energy of formation can be positive or negative depending on the substances.